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REPORT DOCUMENTATION PAGE

DTIC ELECTE NOV 23 1988 H

1a. REPORT SECURITY CLASSIFICATION: Unclassified	1b. RESTRICTIVE MARKINGS
2a. SECURITY CLASSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT: Approved for public release; distribution unlimited.
AD-A202 274	5. MONITORING ORGANIZATION REPORT NUMBER(S): ARO 22572.1-CH
6a. NAME OF PERFORMING ORGANIZATION: Clarkson University	6b. OFFICE SYMBOL (If applicable)
6c. ADDRESS (City, State, and ZIP Code): Division of Research, Potsdam, NY 13676	7a. NAME OF MONITORING ORGANIZATION: U. S. Army Research Office
	7b. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211
8a. NAME OF FUNDING/SPONSORING ORGANIZATION: U. S. Army Research Office	8b. OFFICE SYMBOL (If applicable)
8c. ADDRESS (City, State, and ZIP Code): P. O. Box 12211, Research Triangle Park, NC 27709-2211	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER: DAAG29-85-K-0131
	10. SOURCE OF FUNDING NUMBERS: PROGRAM ELEMENT NO. / PROJECT NO. / TASK NO. / WORK UNIT ACCESSION NO.

11. TITLE (Include Security Classification): Hole Formation (Etching) in Polymers by Far (Deep) UV High Intensity Laser (Eximer) Radiation Pulses and Its Relevance to Photoresists in Deep UV Photolysis of Polymers

12. PERSONAL AUTHOR(S): Jellinek, HHG (deceased), Partch, R. and Kachi, H.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Final	FROM 85/05/01 TO 87/12/31	88/10/20	37

16. SUPPLEMENTARY NOTATION: The view, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy, or decision, unless so designated by other documentation.

17. COSATI CODES		
FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number): Eximer Laser, Polymer Degradation, Polymer Ablation, Polymer Photolgsis

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

Pulsed eximer laser light (193nm) has been used to study the photo and thermal induced degradation (ablation) of six common, industrially important polymers. A spoon gauge was employed to determine the rate of loss of gaseous products from a film. Optical microscopy allowed visualization of the changes that take place in the polymer near the site of hole formation. Little correlation was observed between the depth of holes generated and ave. pulse power or total energy applied. Temperature increases in the polymer film were monitored during irradiation. An attempt was made to correlate calculated and experimental ejection velocities of oligomer fragments of polymer formal by irroliation. The amount of such "sputtered" material is small as opposed to gaseous products. Correlation were made between the percent transmission of infrared light through each type of polymer and the number of pulses.

20. DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
☐ UNCLASSIFIED/UNLIMITED ☐ SAME AS RPT. ☐ DTIC USERS	Unclassified
22a. NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code) / 22c. OFFICE SYMBOL

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HOLE FORMATION (ETCHING) IN POLYMERS BY FAR (DEEP) U.V. HIGH INTERISITY LASER (EXIMER) RADIATION PULSES AND ITS RELEVANCE TO PHOTORESISTS AND DEEP U.V. PHOTOLYSIS OF POLYMER

FINAL REPORT

BY
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October 20, 1988

U.S. ARMY RESEARCH OFFICE

CONTRACT NO. DAAG29-85-K-0131

CLARKSON UNIVERSITY
POTSDAM, NY 13676

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Final Report - DAAG29-85-K-0131

Prepace

The titled research project was envisioned by H.H.G. Jellinek as a natural continuation of his prolific works on polymer degradation. His reputation as an expert on the kinetics of photolytic and thermal degradation extended world-wide. Professor Jellinek unfortunately suffered a serious heart attack during the first few months of the grant period. The research was continued for a second year through the capable laboratory work of Professor Jellinek's long time research associate Dr. H. Kachi, and the interim direction of Professor R. Partch, also of Clarkson University. Professor Jellinek died in 1986 and the termination of the project was further complicated when Dr. Kachi also developed a serious heart ailment at the close of the contract period. This report is therefore not only the final one for the project but also one that closes an era of productive scientific endeavor by Professor Jellinek.

Apparatus and Polymers Employed

1. Major equipment utilized:

a) Lambda Physik Eximer Laser type EMG 100 MSC. Characteristions of the instrument are: wavelength of emitted light, 193nm; pulse energy, 100-200 MJ; ave. power, 5w; max. pulse rate, 50Hz; pulse width, 17ms.

b) Quartz Spoon Gauge (see Figure 1)

2. Polymers Studied: Poly(methylmethacrylate) (Plexiglass), Poly(imide) (Kapton), Poly(carbonate), Poly(styrene), Poly(propylene) and Poly(ethyleneterephthalate).

Results and Discussion

1. Poly(methylmethacrylate) (PMMA).

a) Preliminary studies

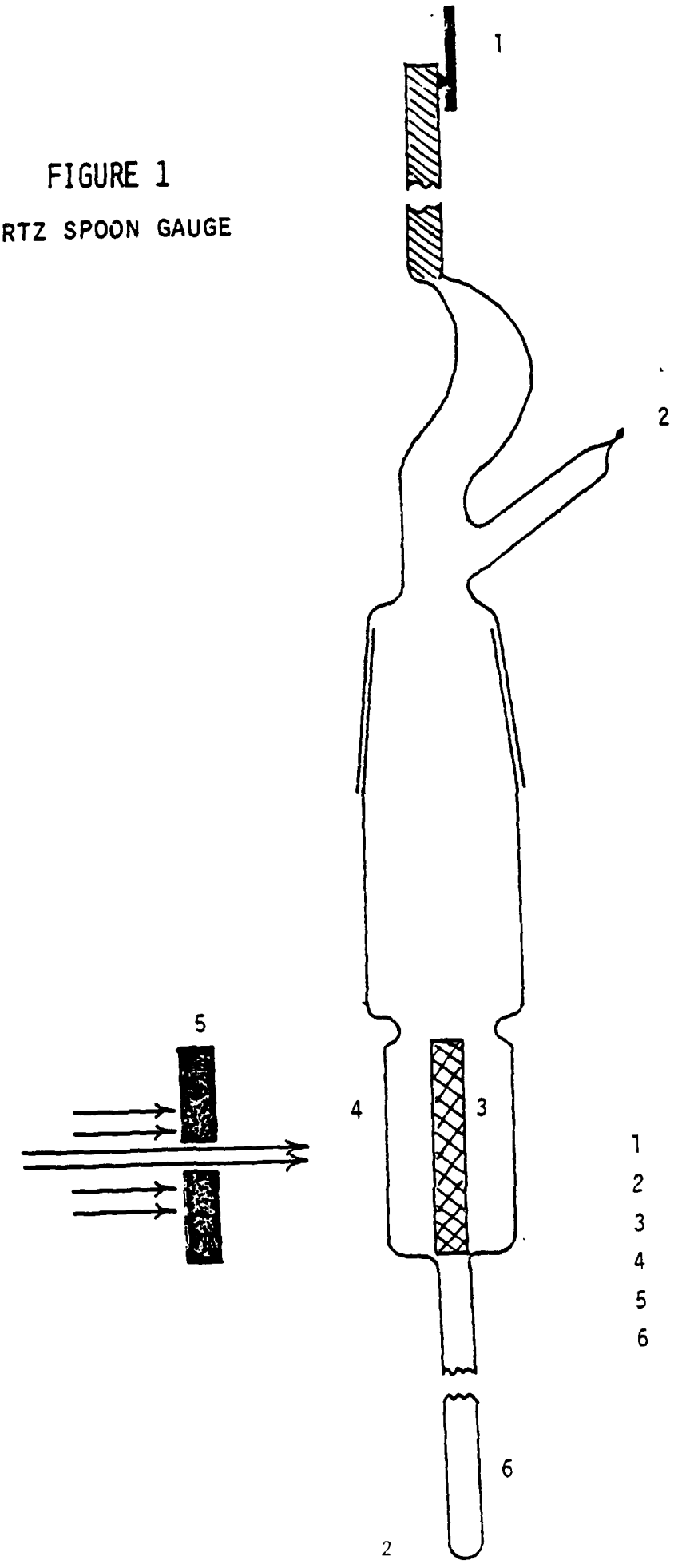
The feasibility to use a spoon gauge, shown in Figure 1, to measure rapid pressure changes due to degradation of polymer [1] irradiated with an eximer laser was examined. With a beam energy of 114mJ/cm^2 PMMA can be etched at a rate of about 1.5 μm depth per pulse [2]. When the PMMA sample was irradiated by the laser through a 0.5cm hole in a metal plate, 8.42 x 10^{-4}mL (NTP) monomer per pulse was produced (assuming all decomposition leads only to monomer). The volume of the spoon gauge is 23.3mL and its sensitivity 0.85±0.2 mm Hg. Irradiation of PMMA at 1Hz for one hour, or for 3600 pulses, produced a pressure change of 79.4 mm Hg at 20^{o}C. The depth of the hole etched in the PMMA films was 540μ, equal to a weight loss of 0.0126 g.

The temperature increase of the PMMA film on a quartz disk with the thickness of 0.05 cm during irradiation by laser was calculated using the following characteristics:

Heat of Polymerization of methylmethacrylate (MMA)	577 J/g.
Heat of Vaporation of MMA	ca.418 J/g.
Thermal Conductivity of PMMA	1.93x10^{-3}J/(sec.)(cm^2)(^{o}C/cm)
Heat Capacity of PMMA	10.55 J/g^{o}C at 300^{o}C

FIGURE 1

QUARTZ SPOON GAUGE



1 Probe of Transducer
2 Vacuum seal
3 PMMA sample
4 Quartz window
5 Iron plate
6 Cold trap tip

The average power of the laser was 4.9$\bar{w}$ under 50Hz pulsation, which was measured by a thermophile detector, Model 25A made by Optical Engineering Inc. When the PMMA film was irradiated by laser 1Hz through a hole with the diameter 0.5 cm, the average power applied to the film was $1.09 \times 10^{-2} \bar{w}$, assuming that the PMMA film adsorbs 100% of laser energy. The loss of heat is primarily due to depolymerization of polymer, evaporation of monomer produced by decomposition of polymer and the conduction of heat through the polymer to a quartz substrate which has ca. 60 times larger thermal conductivity than that of PMMA. From the value of $1.09 \times 10^{-2} \bar{w}$ is substracted the heat of depolymerization ($0.20 \times 10^{-2} \bar{w}$) and heat of evaporation ($0.14 \times 10^{-2} \bar{w}$). The rest of the heat is transmitted by conduction through the film with the rate of $0.76 \times 10^{2} \bar{w}/^{o}C$. If the temperature difference between the surface and the bottom of the coat is 10^{o} C, the rate of conduction is $7.6 \times 10^{-2} \bar{w}$, which is large enough to dissipate heat by laser up to the pulsation ca. 6Hz. In other words, no accumulation of heat significant enough to affect the pressure measurement by a spoon gauge occurs. However, according to the pulsation of high power laser during an extremely short period, such as 17ns, the surface of polymer and the temperature gradient between the surface and the inside of polymer could be as large as $300^{o}C/10$ Å.

b) Weight loss during hole formation at atmospheric pressure.

A 3.0mm thick sample of commercial Plexiglass was irradiated by a far UV laser beam having a diameter of 0.5 cm. The average power was 2 watts/50H_z repetition rate. An attempt was made to continuously monitor weight loss during irradiation using a transducer coupled to a Sanborn recorder equipped with a model 350-1100 B Carrier preamplifier. Unfortunately the minute changes in weight as a function of time were less than the maximum sensitivity of the transducer. However, using an analytical balance, we determined that 0.18 mg of sample was lost after irradiation at 3 H_z for 5 minutes plus 10 H_z for 45 minutes. This corresponds to the formation of a hole 7.7 µm deep and 0.5 cm in diameter. Photograph 1 (750 x magnification on all photographs) shows nonuniform craters at random locations in the region where the beam impinged on the sampie.

c) Effect of vacuum on hole formation

Far UV laser pulses not only are capable of causing photochemical degradation of polymer to monomer (gaseous) and oligomer fragments, but also causes the sample to be heated, even to some softening temperatures. The latter in the case of PMMA is around $150^{o}C$, which is considered to be the lowest temperature at which the plastic will be molten enough to flow. We have found that when a sample of PMMA is irradiated with far UV pulses under vacuum in the spoon gauge a phenomenon occurs much different than that observed in air. Not only is there some hole formation where the light strikes the sample but also a large number of voids ranging from 1-25 µm in diameter are created near and below the surface of the polymer around the hole. These can be seen in photographs 2-4. We believe these voids are formed when photodegradation releases gaseous products in a region of the polymer where the temperature has reached at least $150^{o}C$. As the gas attempts to escape into the surrounding vacuum physical disturbances in the polymer occur. Notice how photograph 1 of a sample irradiated in air differs from photographs 2-4. By using different focus points of the optical microscope we have approximated the depth of the voids formed in PMMA.

The data in Table 1 shows that the depth to which voids are formed has no strict correlation with either average power (Figure 2) or with duration of irradiation. However, a plot of total energy applied versus void depth (Figure 3) shows a trend that we suspect will have a much higher correlation coefficient as we refine our ability to experimentally evaluate the deepest level in the polymer that voids occur in a specific experiment. If our assumption is correct, that void formation is the result of both the chemical photodegradation of polymer to monomer and the thermal heating of the bulk polymer to a flowable mass, we believe we have found a way to evaluate more precisely than before the heating that takes place during polymer ablation. This technique should equally apply to processes that occur when other materials such as

PHOTOGRAPH 1

PHOTOGRAPHS 2-4

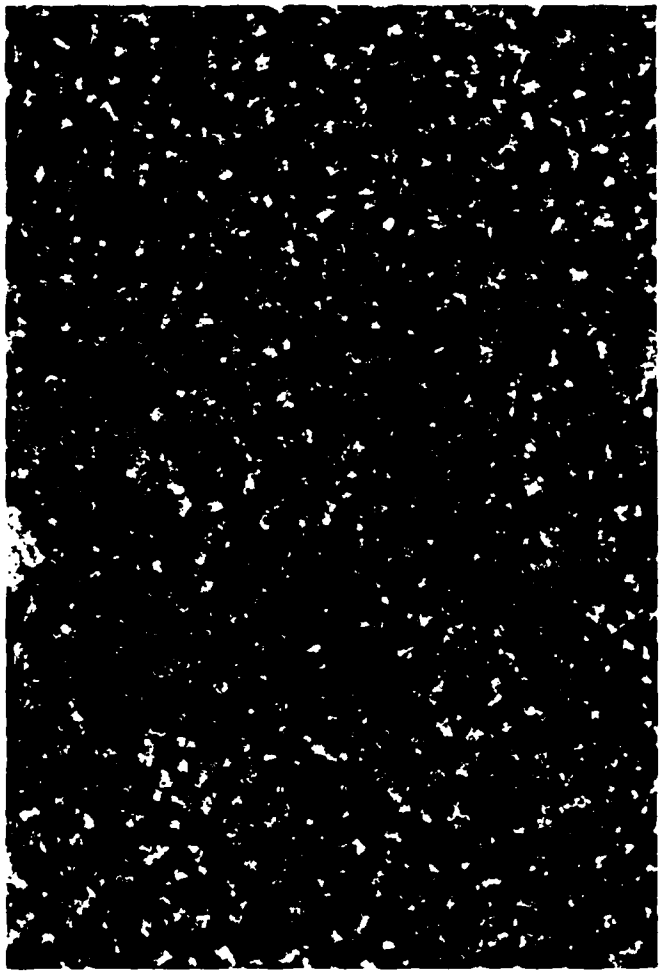


TABLE 1

Exp. No.	PMMA Sample g	Repetition Rate Hz	Duration of Irradiation, mins	Average power, $\bar{w}$ (mean value)	Total energy applied to PMMA J	Depths of Voids μm
1	1.66899	5	45	3.1	149	25
2	0.92488	2	80	3.6	120	23
3	0.66864	1	125	3.9	107	10
4	0.93370	2	90	3.8	145	10
5	0.88957	3	60	4.6	180	14
6	0.66691	5	45	4.5	217	18
7	0.66123	5	45	4.4	212	14
8	0.65039	5	45	4.7	226	23
9	1.18109	3	93	4.0	239	19
10	.076875	4	55	4.1	194	15

FIGURE 2

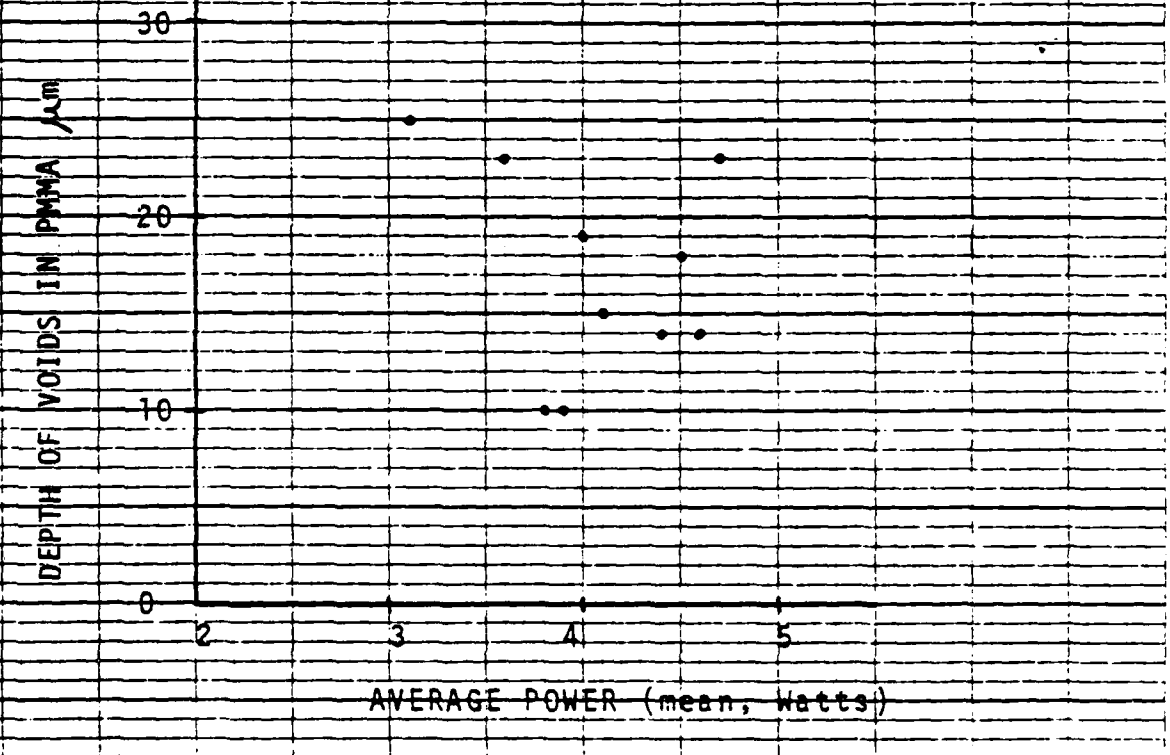
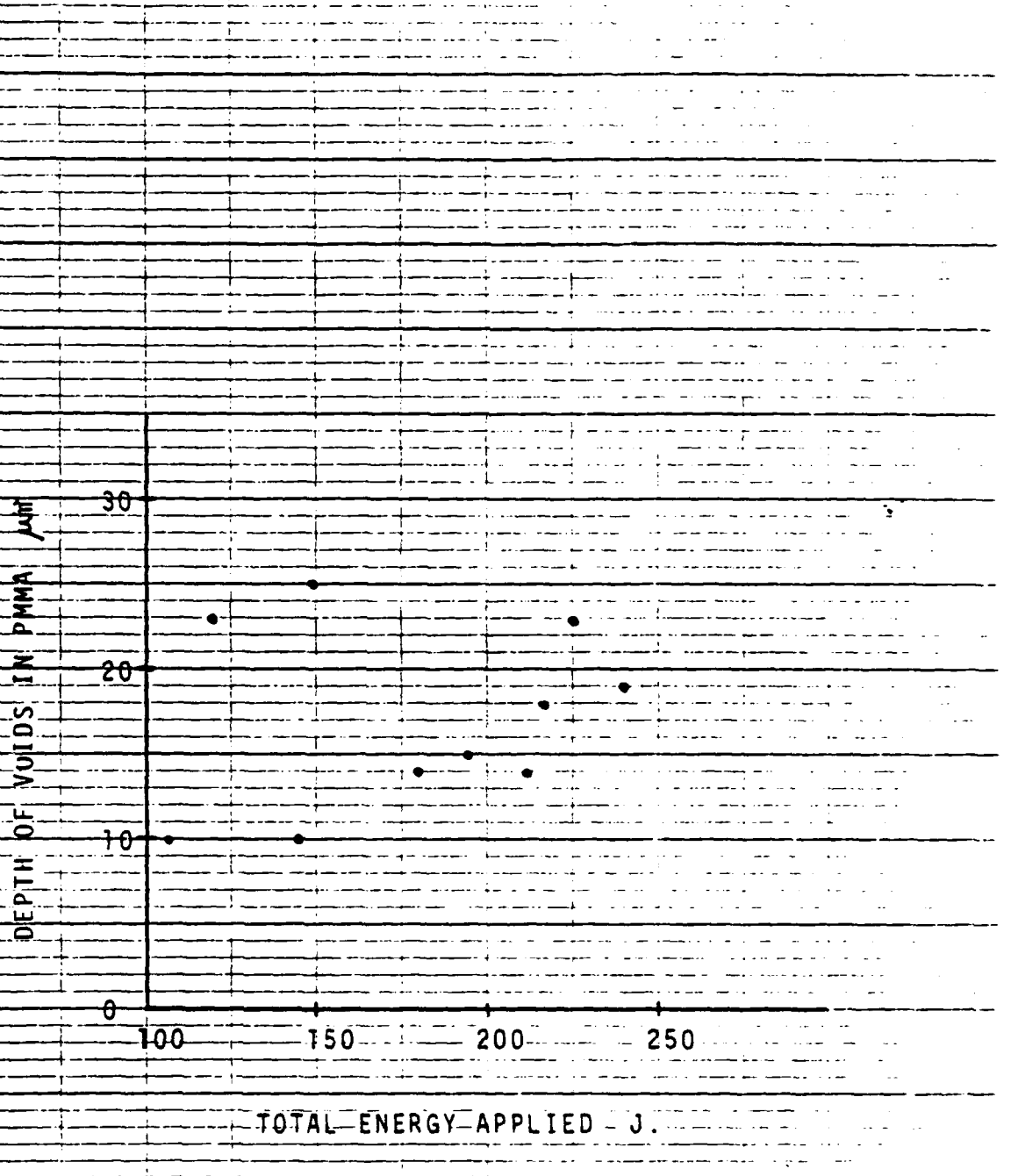

30
20
10
0
DEPTH OF VOIDS IN PMMA μm
2
3
4
5
AVERAGE POWER (mean, Watts)

FIGURE 3

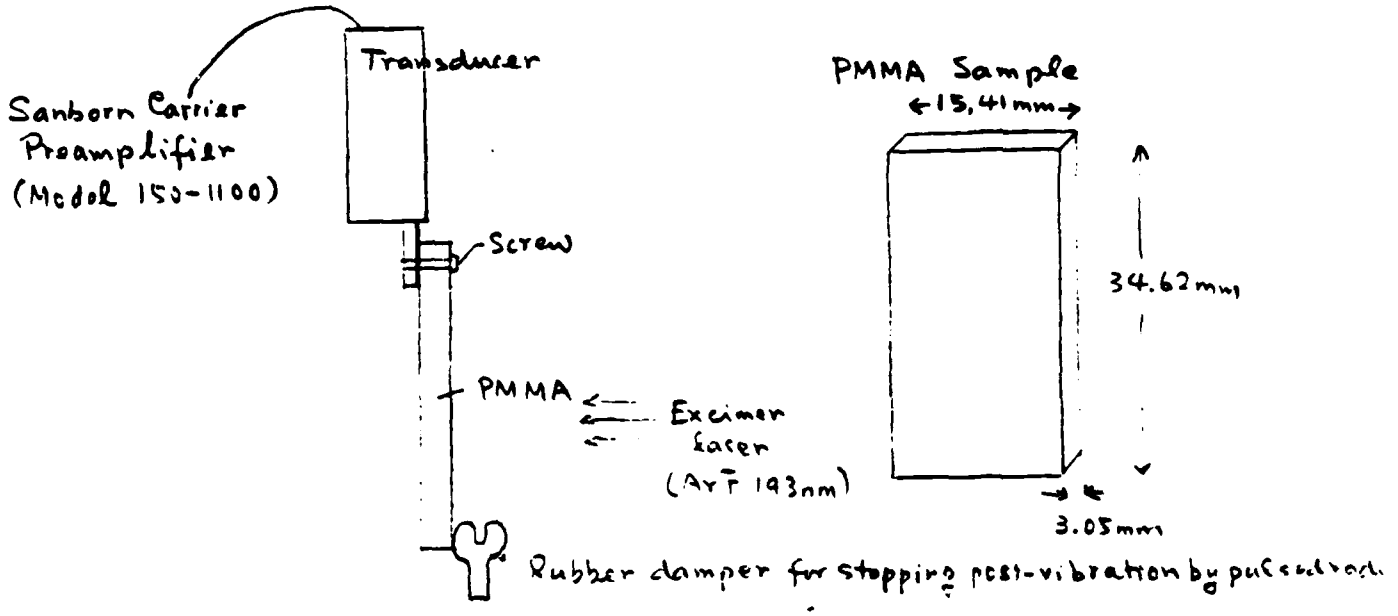

DEPTH OF VOIDS IN PMMA μm
30
20
10
0
100
150
200
250
TOTAL ENERGY APPLIED - J.

polycarbonates and polyethylenerephthalates are irradiated.

The rate of ablation of PMMA in a vacuum is not only due to photodegradation of polymer to volatile monomer and oligomer fragments, most of which are ejected as gases, but also to sputtering. This contrasts the work of others who have studied ablation at atmospheric pressure. The degree of sputtering that contributes to hole formation can be monitored using the spoon gauge because the quartz windows of the gauge, which can be viewed (Photograph 5) through a microscope, acts as a collector for the particles being ejected from the PMMA surface. The sputtered particles that fall within the 0.5 cm diameter beam of light on the quartz windows, and the carbon formed from their further decomposition, reduced the transmission of energy to the PMMA sample. As a result, only initial rates of ablation of gaseous products, as measured by pressure changes occurring in the spoon gauge over time, are plotted in Figure 4. Our data in Table 2 and Figure 5 corroborates but also differs from literature data that there is a correlation between rate of ablation and fluence. Our values are much lower.

d) Ejection velocity of products by ablative decomposition

An experiment for measuring the ejection velocity of particles was carried out by using a transducer for measuring repulse force due to eject particles. Experimental set-up is shown below.



PHOTOGRAPH 5

FIGURE 4

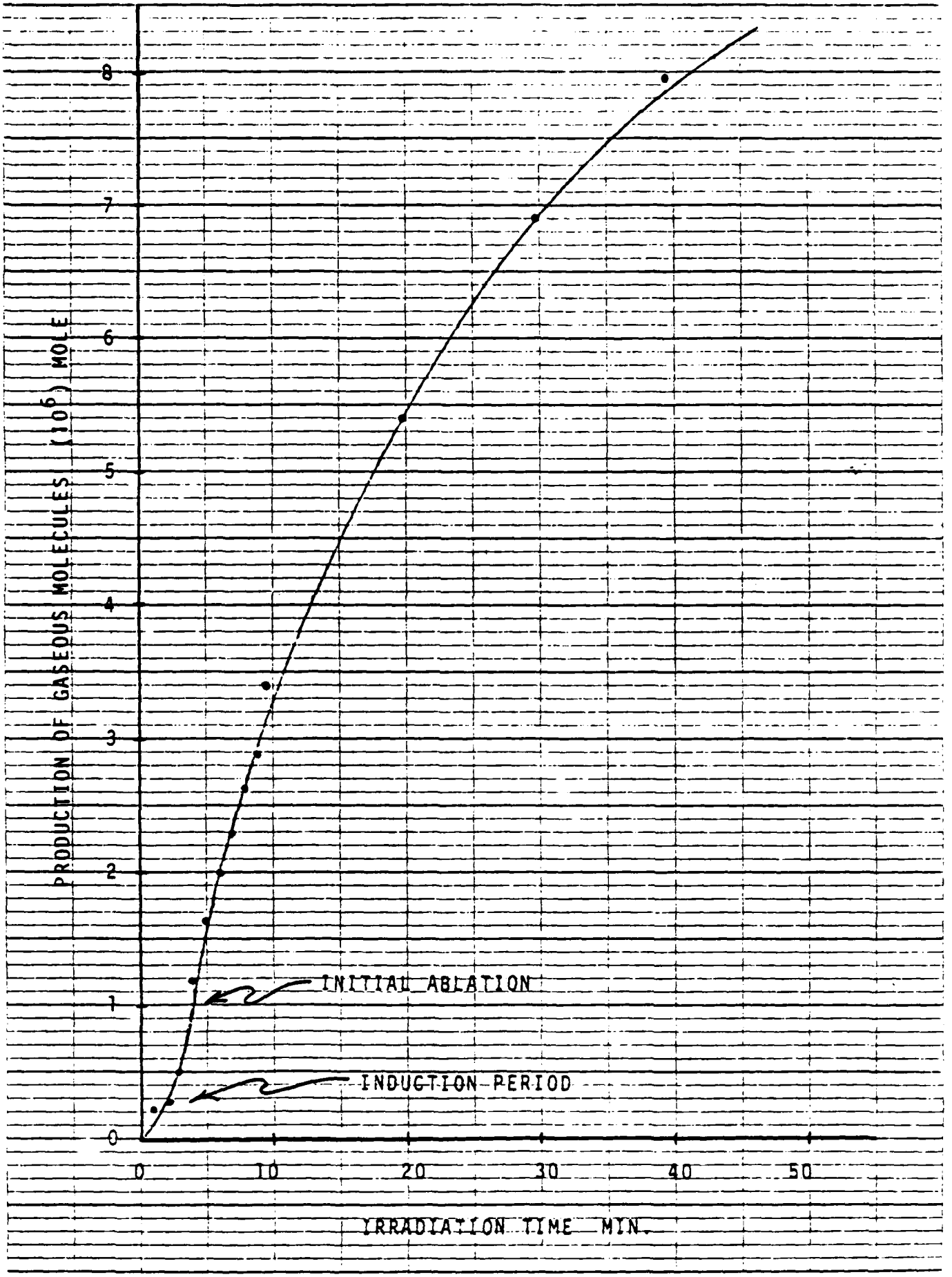
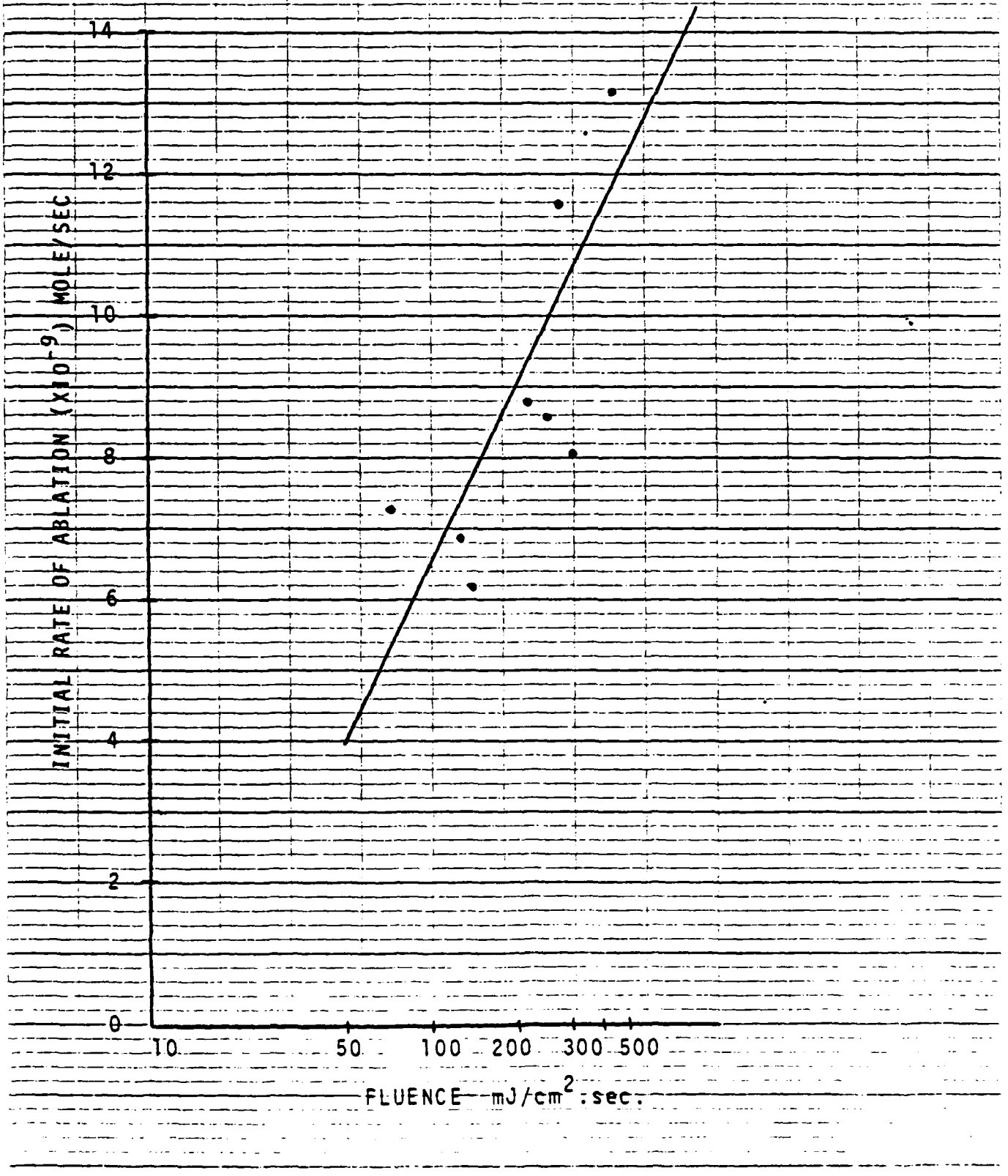

PRODUCTION OF GASEOUS MOLECULES (10^6) MOLE
0
1
2
3
4
5
6
7
8
INITIAL ABLATION
INDUCTION PERIOD
0
10
20
30
40
50
IRRADIATION TIME MIN.

Table 2

Exp. No.	Repetition rate H_z	Initial rate of ablation X 10^{-8} mole/sec.	Fluence mJ/cm^2 sec.
3	1	0.76	73
2	2	0.69	127
4	2	0.62	137
9	3	0.88	218
5	3	0.86	255
10	4	0.81	300
1	5	1.16	281
8	5	1.32	427

FIGURE 5


INITIAL RATE OF ABLATION (X10^{-9}) MOLE/SEC
14
12
10
8
6
4
2
0
10
50
100
200
300
500
FLUENCE—mJ/cm^2.sec.

The velocity, υ; of ejected particles was calculated by using an equation $F\Delta t=m\upsilon$ where F=the average force acting during the time Δt

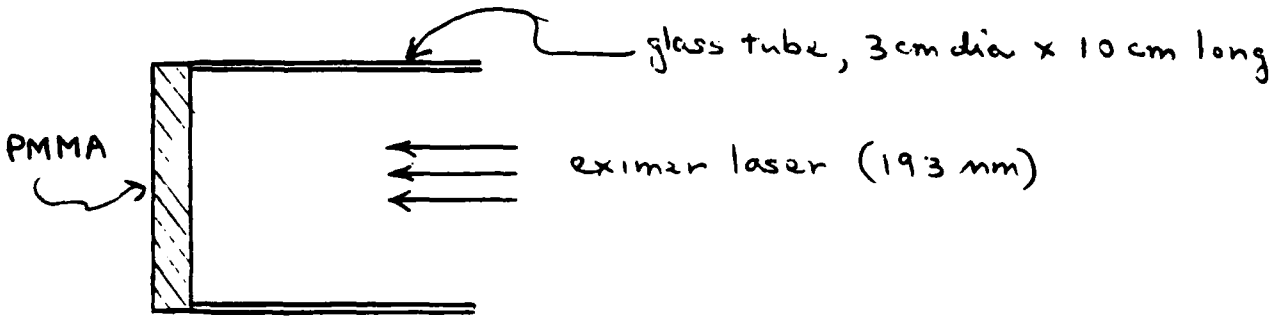
m=ejected mass $\Delta t=17\times10^{-9}$sec.

Exp. No.	Pulse Energy	Average Power	Pulsation Rate	$\bar{F}$	m	υ cm/sec
1	156mJ	4.8$\bar{W}$	0.77Hz	41 dyne	8.33×10^{-6}g	8.5×10^{-2}
2	169mJ	5.9$\bar{W}$	0.98Hz	45 dyne	8.23×10^{-6}g	9.4×10^{-2}

Unfortunately, the combined response of preamplifier, drive amplifier and galvanometer is in the 5msec. range, which is too long compared to 17nsec. pulsation. Hence the method is not able to measure the velocity of particles produced by pulsed radiation.

e) Determination of sputtered polymer particles produced by pulsed radiation

The following experiment was carried out in attempt to make more accurate measurements on the sputtering of particles from PMMA film.



Radiation Conditions: Pulse Energy 156mJ

Average Power 5.7$\bar{W}$

Pulsation Rate 2Hz

Duration of Radiation 2 hrs.

Total Pulses 14,400

Results: wt. Loss of PMMA 0.06658g

Sputtered polymers 0.00139g 2.1% of PMMA

The amount of sputtered polymer was small and hence it is not major product by irradiation (ablative decomposition).

f) Etching rate vs number of pulses

As shown in Figure 6, the etch rate of PMMA is reduced remarkably with increase of the number of pulses. Especially drastic changes occur at the early stage of radiation. The etch rate is decreased over 80% after 8000 pulses.

In the thermal decomposition of PMMA at lower temperature such as 300^{o}C, the depropagation chains are predominantly end-initiated and chain termination occurs mainly by bimolecular termination. However, at higher temperature such as 500^{o}C, initiation is predominantly by random chain scission and the majority of chains are effectively terminated as the depropagation reaches the end of the molecular chain, and the terminated radical distills out of the system. It has been reported that at ca. 500^{o}C random chain scission followed by complete unzipping (depropagation) occurs. Thus, the experimental rate constant (kir) was directly proportional to Dp (Degree of polymerization).

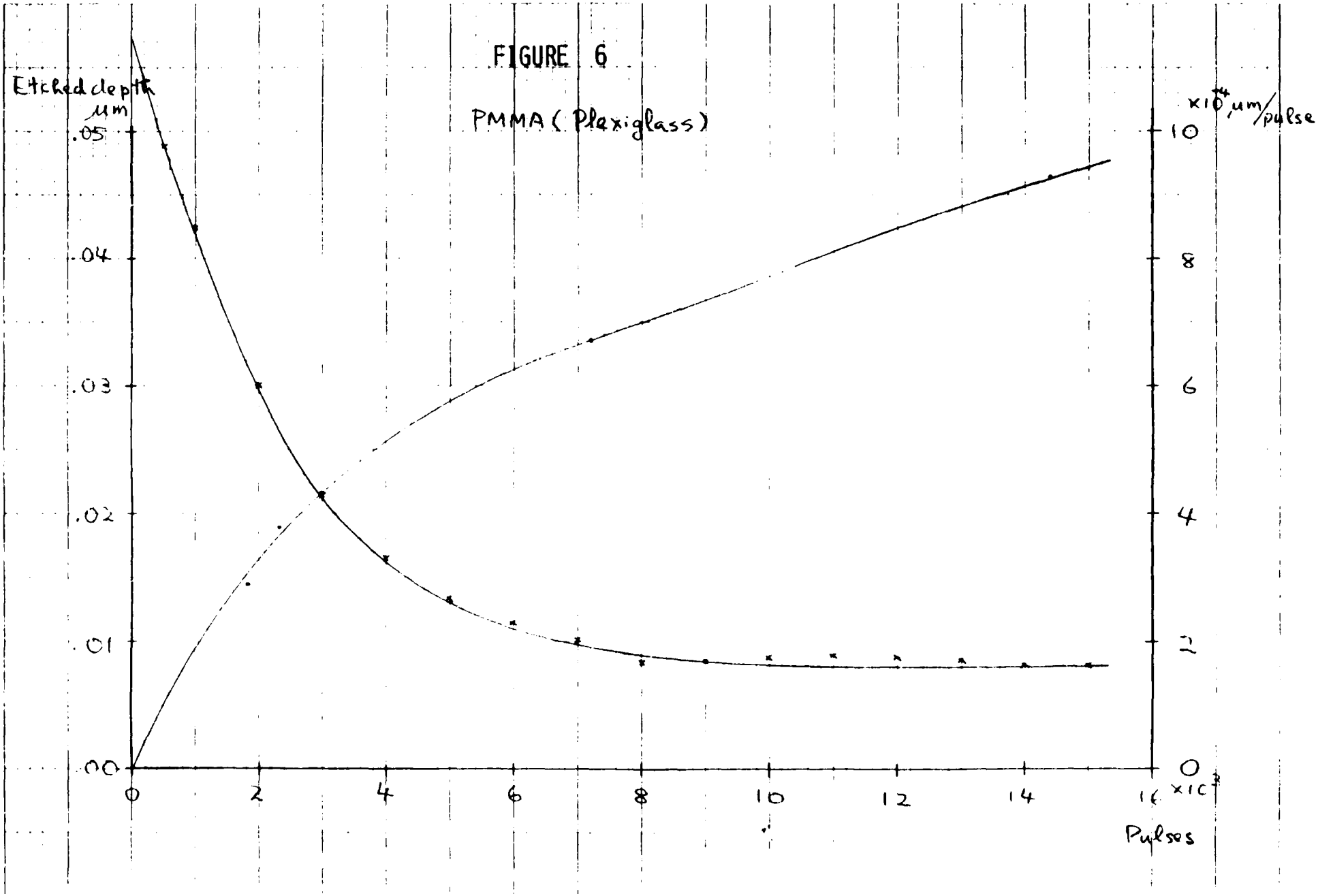
$$-\frac{dw}{dt} = 2KirDpW$$

where W: weight of polymer at time t.

PMMA is expected to be heated to over 2000^{o}C by radiation of ArF excimer laser pulses of 17ns. Therefore the degradation of PMMA would be a type of random initiation followed by complete unzipping. Simultaneously, PMMA degrades by the same mechanism when exposed to radiation of 193nm uv light. Hence, degree of etching of PMMA is reduced and reaches a constant value at an equilibrium state which is shown in figure after 8000 pulses.

FIGURE 6

PMMA (Plexiglass)



2. Susceptibility of different polymers to ablation and effect of irradiation on the infrared transmission of their films

a) General Experimental Procedure

A polymer film sample was prepared and mounted on a cell for infrared spectroscopy and irradiated (193mm) in air at 20°C by ArF eximer laser for a certain time. Immediately before and after irradiation the weight of the film sample was measured by a balance having sensitivity ±0.01mg.

The percent transmission of infrared light at an appropriate wavelength through the film was monitored (Beckman Microspec Spectrometer) as a function of number of pulses.

The temperature rise in polymer films during irradiation was measured by placing a 1-mil thermocouple between films mounted in the cell. Due to the long 50 msec response time compared to the 17 msec pulse width of the laser, and the size of the thermocouple compared to the etched depth, these measurements were considered to be qualitative only.

b) Ablative Decomposition of PMMA

Preparation of PMMA Film

Polymethylmethacrylate (PMMA, Intrinsic Viscosity 1.3, Polysciences Inc.) (25g) was dissolved in acetone (10mL). Film was prepared by flow-coating the solution on a glass plate and drying first at 20°C and then at 70°C under 0.025 torr vacuum for 12h. The film was stored in a desiccator ($CaC1_2$) until used.

Results of Radiation Experiments

Table 3-(1) and Figure 7 show the results of irradiating PMMA film at a pulse rate of 2.92 Hz. In general, a film sample irradiated for a longer period contained more bubbles in and around the exposed area. The etching rate was independent of the etching period, i.e., the etched depth as shown in Figure 7.

From Table 3-(2) one obtains an etched depth/pulse of 0.103± 0.008μm at an incident fluence of 139 J/cm^2. This compares to a value of 0.17μm reported in the literature [3]. We also observed that when irradiated for 10 minutes the film has a hole through it equal to about 5% of the total irradiated area. The polymer film at the edge of the hole was melted. This means that the etched depth at the hole was more than the original film thickness (1.07mm) which was about 6.2 time larger than the etched depth calculated from weight loss. Therefore, the value of the etched depth is dependent on the method of measurement.

The rise in film temperature during irradiation is shown in Figure 8. Qualitatively, the value increased rapidly and levelled off near 100°C at about the same time the hole through the film formed. Of course the measured temperature was a value equalized over all the polymer film surrounding the tip of the thermocouple.

Using a value of 10.55 $KJKg^{-1}K^{-1}$ at 300°C for the heat capacity of PMMA, it can be calculated that a film 0.103μm thick, when irradiated with one pulse from the ArF eximer laser, should be heated to 1021°C (neglecting heat of depolymerization (57.8KJ/mo1) and thermal conductivity for 17 nsec.

It is well known that the photolysis of PMMA results in a random chain scission by a radical process. On the other hand, thermal degradation is much more ordered and starts at

TABLE 3-(1)

Irradiation Time	Average Power	Total Power Applied	Incident Fluence, Fo	
Mins.	$\bar{w}$	$\bar{w}/cm^2$	mJ/cm^2	ℓn Fo
1	4.78	0.66	147	4.99
2	4.74	1.31	146	4.98
3	4.70	1.95	145	4.97
4	4.64	2.57	143	4.96
5	4.58	3.17	141	4.95
6	4.50	3.74	138	4.93
7	4.42	4.28	136	4.91
8	4.34	4.81	134	4.89
9	4.25	5.30	131	4.87
10	4.15	5.75	128	4.85
Average	4.51 ± 0.22		139 ± 7	4.93 ± 0.05

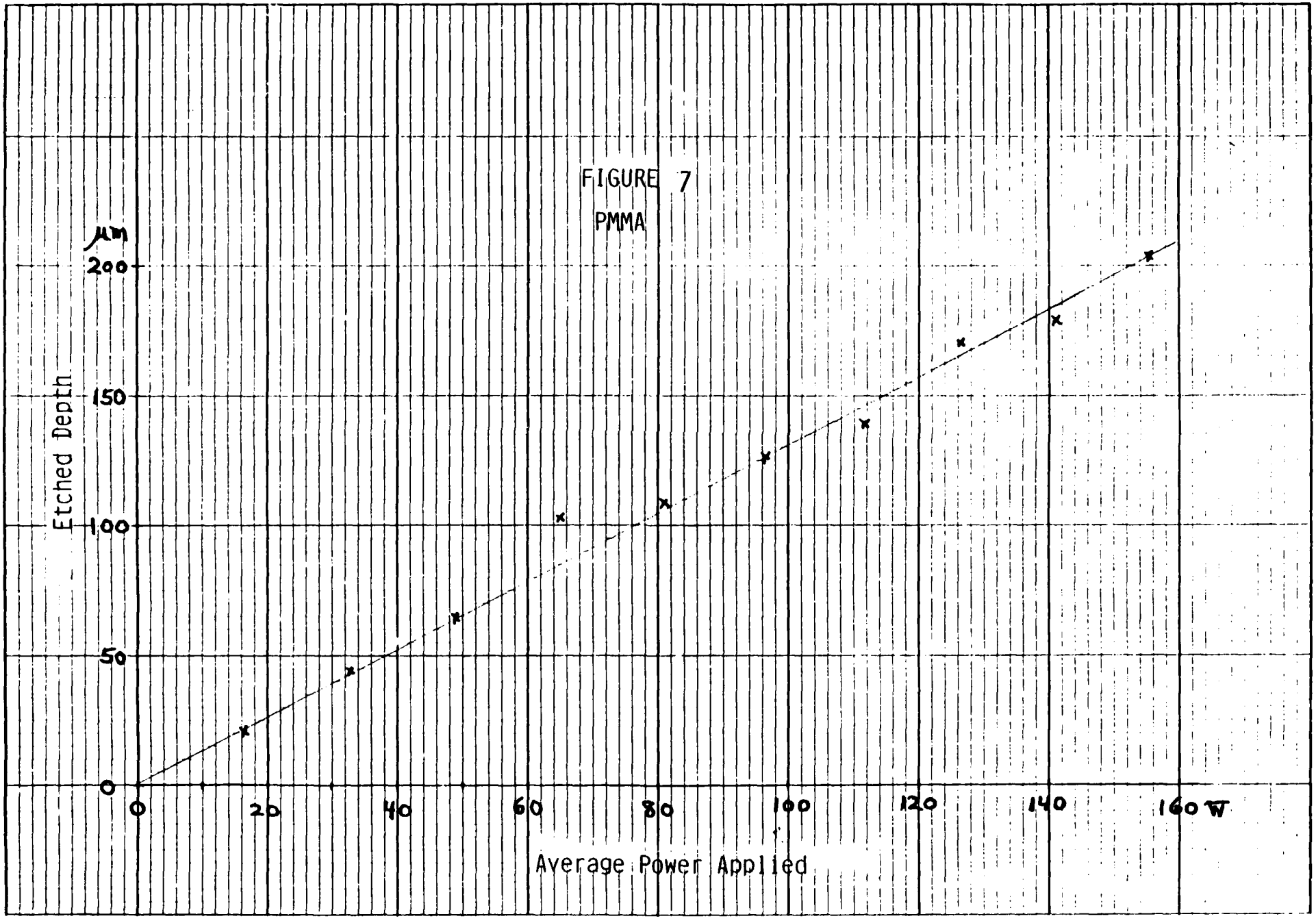


FIGURE 7
PMMA
Etched Depth
μm
200
150
100
50
0
0
20
40
60
80
100
120
140
160 W
Average Power Applied

TABLE 3-(2)

Irradiation Time	Film Thickness	Weight Loss	Etched Depth	Etched Depth/Pulse
Mins	mm	mg	μm	μm
1	0.91	2.76	17.8	0.102
2	1.22	5.69	36.8	0.105
3	0.86	8.47	54.8	0.104
4	1.20	13.35	86.3	0.123
5	1.16	14.07	91.0	0.104
6	0.91	16.50	106.7	0.102
7	1.16	18.05	116.7	0.095
8	1.29	22.25	143.8	0.103
9	1.28	23.19	149.9	0.095
10*	1.07	26.60	171.9	0.098
Average	1.11±0.16			0.103±0.008

*Film had a hole through it.

FIGURE 8

CITADEL NO 642 - CROSS SECTION - 10 SQUARES TO INCH

a chain end. The latter "unzipping" occurs to produce 100% monomer from PMMA at less than 375°C. It seems clear, therefore, that during irradiation with the ArF eximer laser PMMA can degrade both by photochemical and thermal processes. The balance between these has yet to be precisely established.

Future experiments will be carried out using a KrF eximer laser (248nm). The absorption (log ε) of PMMA is 0.42 and 4.02 at 248nm and 193nm, respectively [4]. Therefore, with less absorption at 248nm the depth of penetration into PMMA should be greater and the temperature rise less. If an absorber dye for 248nm UV is added to the PMMA, the depth of penetration shall be reduced and the film temperature raised. It is proposed that the rate and mechanism of etching can be controlled by changing the concentration of the absorber. In this way sharply etched shapes may be achievable.

c) Ablative Decomposition of Kapton

Kapton film (3 mil) was supplied by R. Srinivasan, Watson Laboratory, IBM and used as received.

Results of Radiation Experiments

Table 4 and Figure 9 show the results of irradiating Kapton film at a pulse rate of 3Hz and average power of 5.1$\bar{w}$. Unlike PMMA, Kapton film decomposed to produce carbon particles on the surface as well as hole formation. The build up of carbon during an experiment reduced the transmission of laser light directly to the polymer. However, because the etch rate was constant it can be assumed that a combination of heat and light energy was sufficient to cause continual ablation to occur from the film.

Figure 9 and 10 show that when the effect of laser pulses on Kapton is monitored by infrared spectroscopy at 2.5-2.6μm, there is an induction period before major changes in infrared transmission begin to occur. In general, a minimum of 300-400 pulses is needed before changes begin regardless of pulse rate.

Hole depths approximately equal to film thickness of Kapton could be achieved using a pulse rate of 1Hz and average power of 4.5$\bar{w}$ for 26-27 min. This corresponds to an etch rate of 0.0504μm/pulse at an incident fluence of 117mJ/cm^2 (ℓnF=4.77), which compares favorably to the literature value of 0.0603μm/pulse. [3]

The use of 5Hz pulse rate irradiation caused the temperature of Kapton film to rise to about 100°C. Since the etched depth per pulse was about one quarter that of PMMA, one can calculate that the actual temperature of the Kapton film should be much higher than that of PMMA. When Kapton is heated to 950°C in helium a weight loss of 45% occurs and carbon char can be observed. [5] It has been suggested that the thermal degradation of Kapton proceeds by initial cleavage of an imide carbonyl-nitrogen bond. [6] We believe that in our experiments that Kapton is heated to over 400°C in the local vicinity of irradiation.

d) Ablative Decomposition of Polycarbonate (PC)

a) Polycarbonate (Lexan, Grade 100-111, General Electric) was dissolved in dichloromethane and the solution flow-coated on a glass plate. Final drying was carried out at 100°C and 0.025 torr vacuum.

b) Results of radiation experiments.

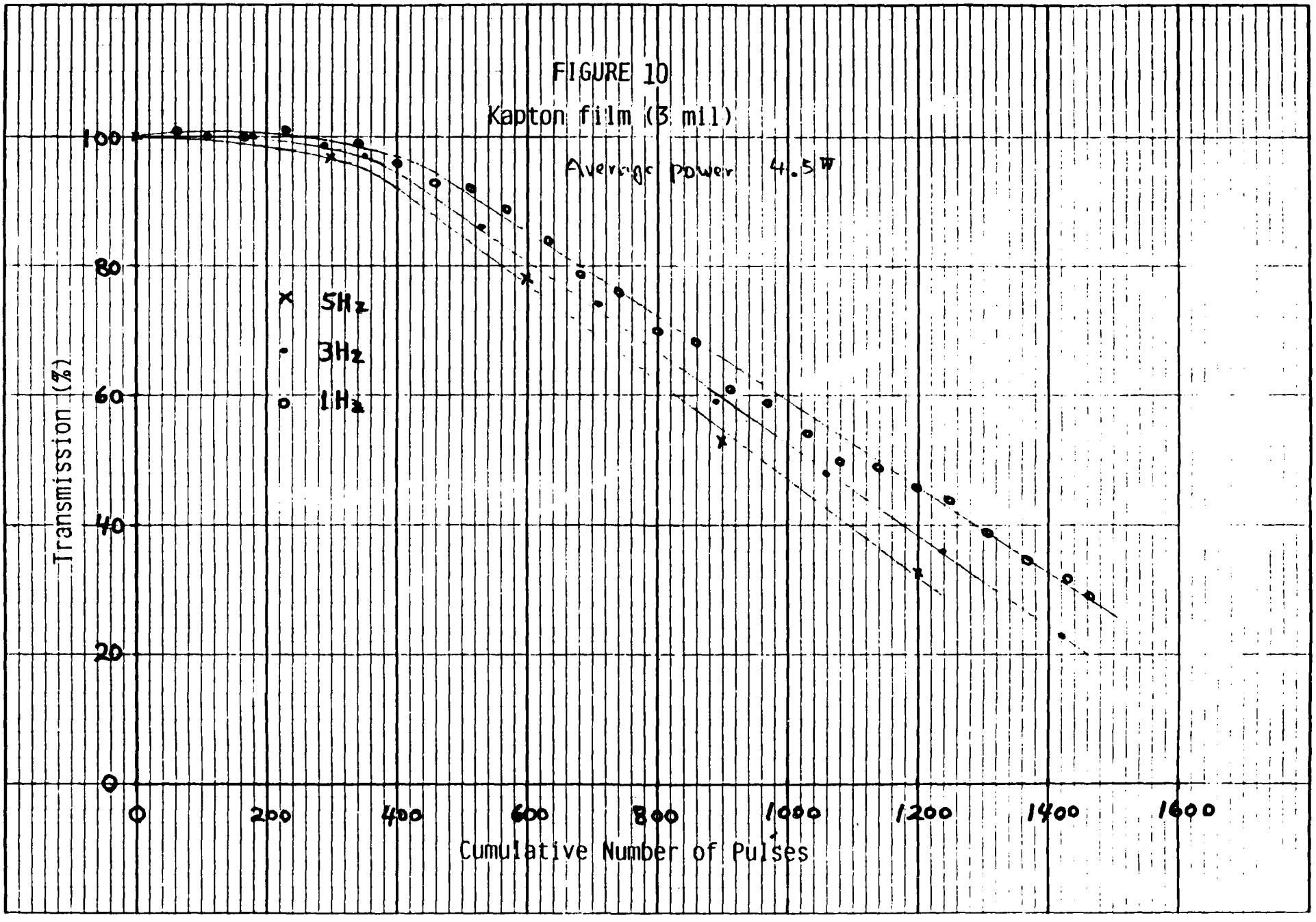
Figures 11 and 12 show the results of irradiating PC at pulse rates of 3 and 1Hz, respectively. Again as with Kapton, hole formation was accompanied by carbon particle

TABLE 4

Irradiation Time	Weight Loss	Etched Depth	Etched Depth/Pulse	Transmission
mins	mg	μm	μm	%
0	--	--	--	100
1	0.41	1.9	0.0106*	99
2	1.60	7.5	0.0208	96
3	3.19	15.0	0.0278	85
4	3.59	16.9	0.0235	68
5	4.95	23.3	0.0259	52
6	5.86	27.5	0.0255	40
Average			0.0247±0.0027	

* This value approaches the limit experimental error and was not included in the average.

CITADEL NO 642 - CROSS SECTION - 10 SQUARES TO INCH



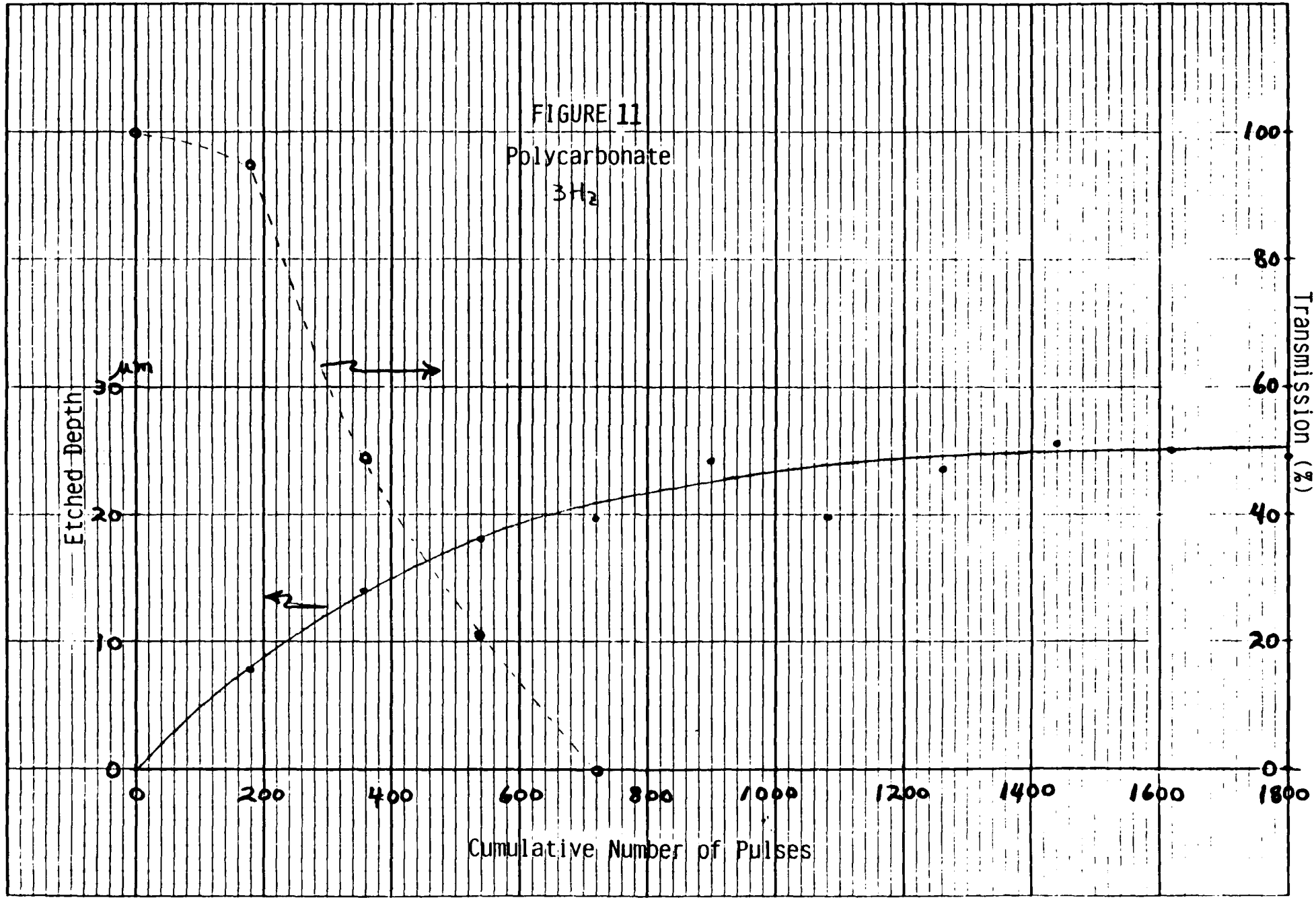
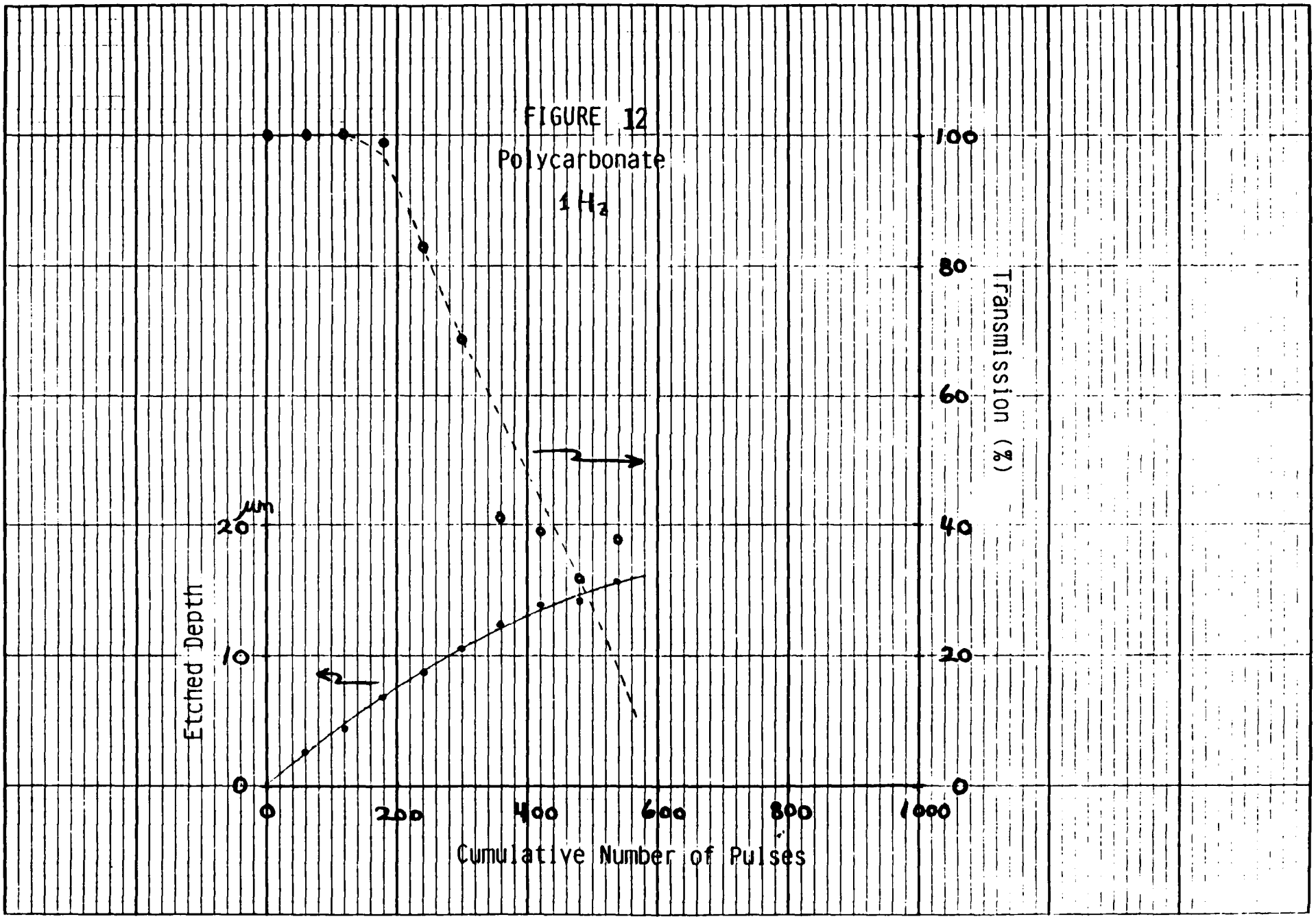


FIGURE 11

Polycarbonate

$3H_2$



buildup. The percent transmission of infrared light (2.95μm) through the film as a function of number of pulses rapidly decreased, but with PC, concomitant with termination of etching. Our values for one minute etched depth per pulse of 0.0439μm - 0.0450μm at an incident fluence of 116 J/cm^2 are smaller than the value 0.070μm reported earlier. [1]

Decreases in transmission and the etched depth in the case of PC are more drastic than for Kapton. Since the etched depth for PC approaches a limiting value after about 800 pulses while that of Kapton is still increasing after 1200 pulses, one may conclude that the carbon particles produced from the degradation of PC by 193nm light are different than those from irradiation of Kapton. Somehow, those from PC neither transmit the light to the remaining, underlying polymer, nor convert the light energy into heat as efficiently.

PC film was irradiated at a pulse rate of 3Hz for one minute with different fluence intensities. The results are shown in Figure 13. Our values versus those from the literature [1] (in parentheses) for the absorption coefficient, β, and the threshhold value in the fluence, F_{TR}, are, respectively: 36.3μm^{-1} (18.49μm^{-1}) and 21.1 mJcm^2 (37.34 mJcm^2). No answer for the discrepency can be offered.

The photodegradation of PC proceeds by random bond breaking at ester linkages without crosslinking. [7] Pyrolysis of PC at 400^{o}C produces considerable amount of CO, CO_2, CH_4, C_2H_6 and C_2H_4. At 500^{o}C, according to IR data, methyl groups disappear, ester groups are significantly reduced and absorption bands corresponding to benzene rings are intensified. [8] However, thermal degradation data of PC in the absence of oxygen are not available.

We plan to carry out experiments to determine if addition of PC to other polymers can serve as a barrier against further etching during lithographic processes.

e) Ablative Decomposition of Polystyrene (PS) and Polypropylene (PP): Preliminary Results.

a) Polystyrene (MW 860,000, MW/Mn=<1.15, PS standard from Mellon Institute) was dissolved in toluene to prepare a 5% solution. This was film case (31μm) and dried at 60^{o}C and 0.05 torr vacuum in 12h. Polypropylene (0.5 mil, 16μm, capacitor grade, Hercules Inc.) was used as received.

b) Results of radiation of PS.

The film was irradiated for 1 min at an average power of 4.2$\bar{w}$ and incident fluence of 97mJ/cm^2. The etched depth was found to be 2.66μm, or 0.0443μm per pulse. The formation of carbon particles was observed but no change in transmission of infrared light through the exposed film as a function of number of pulses was found.

c) Results of radiation of PP.

Conditions in the laser experiments were essentially the same as those for PS. Weight loss of the film was very small and approached the tolerance of the balance. No carbon particle formation was observed.

f) Ablative Decomposition of Poly(ethyleneterephthalate) (PET).

a) Poly(ethyleneterephthalate) film (type S, without additives, 51μm thick) from the Teijin Co. was used as received.

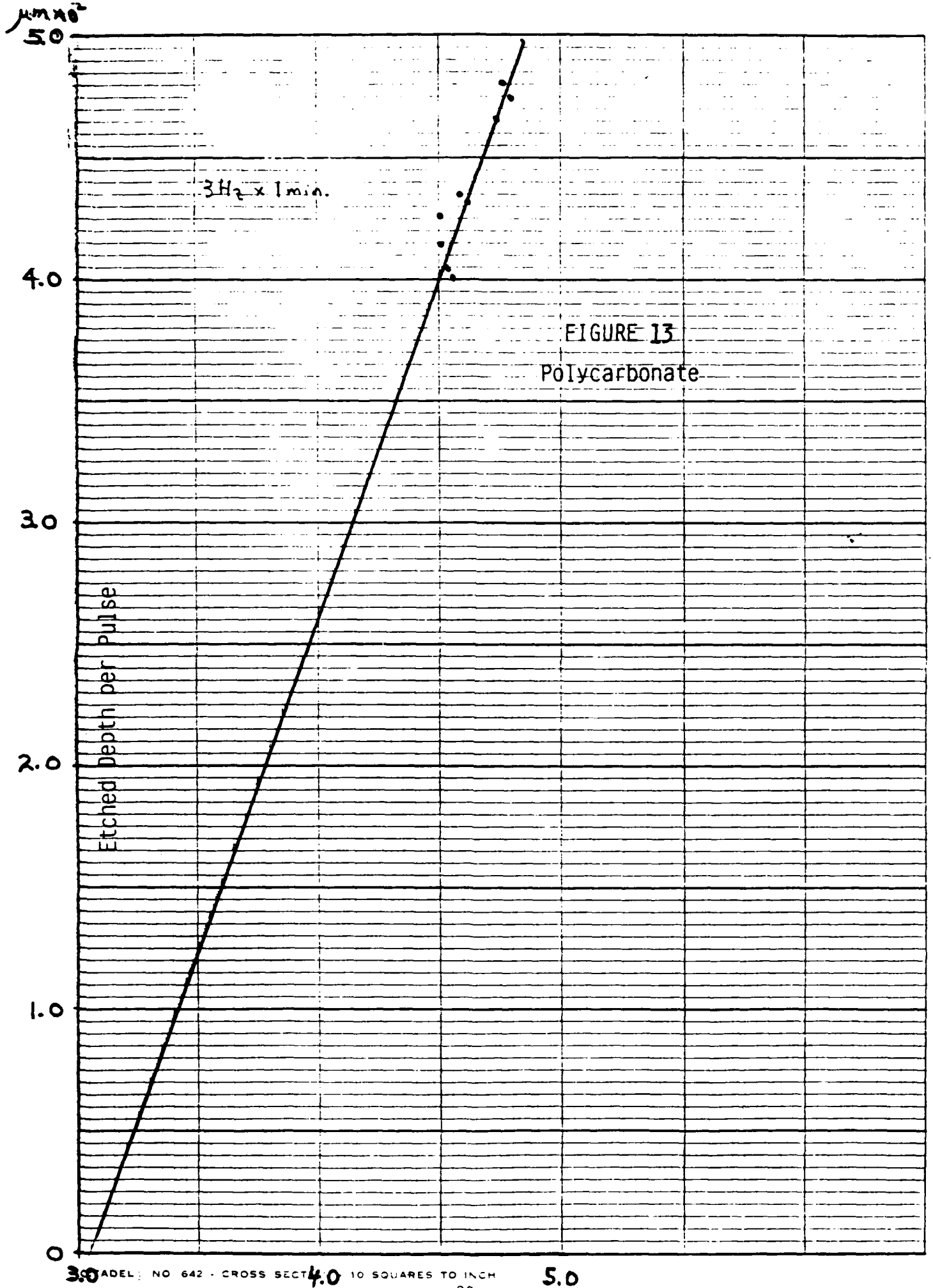


FIGURE 13

Polycarbonate

FIGURE 14

CITADEL NO 642 - CROSS SECTION - 10 SQUARES TO INCH

b) Results of radiation of PET.

Figure 14 shows the results of two runs at a pulse rate of 1Hz. The film became milky colored with time as a result of the formation of terephthalic acid. Since the latter compound absorbs at 193nm the etching process continues even though transmission of 4.17μm infrared light through the film decreases by 60% after only 400 pulses. New infrared absorptions at 2.5-2.6μm (O-H stretch) are exhibited by the irradiated film.

The effect of changing fluence intensity was studied and, as with some of the other polymers, the results of the current experiments do not corroborate earlier data. For instance, when ℓn F is 4.67 and 4.95, the etched depth/pulse was recorded as 0.032 and 0.033μm. An earlier report gives values of 0.065 and 0.085μm for the same conditions.

Conclusion

The results contained in this report demonstrate that various organic polymers readily undergo degradation when irradiated with 193nm pulses of light from an eximer laser. Polymer films do not fragment as cleanly as suggested in the literature. More research using the described processes is necessary before definitive answers to kinetic and chemical questions can be prestulated.

Acknowledgement

The principal investigator thanks the DOD and specifically the Army Research Office for funding and for allowing a delay in preparing the final report due to health problems of personnel involved.

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